

following can be shown: (1) that the process as claimed can be used to make other and materially different product or (2) that the product as claimed can be made by another and materially different process.

As to the first prong, the Group I claims are directed to a nitride semiconductor light emitting device and the Group II claims are also directed to a method of making the identical product recited in the Group I claims. Thus, the process recited in the Group II claims cannot be used to make other and materially different product from device recited in the Group I claims.

As to the second prong, the product claimed in the Group II claims cannot be made by the conventional process because the product made by the present process of the Group II claims is different from a product made by the conventional process.

The conventional process for making p-type GaN comprises: a first step of growing p-type GaN using NH₃ as nitrogen source; and a second step of annealing the p-type GaN for activation by breaking Mg-H complex. The process of the present invention does not need to use the second step to forming p-type GaN by using NH₃ and Hydrazine as nitrogen source. The differences in material property between the convention p-type GaN using activation process and the as-grown p-GaN of the Group I or the Group II are shown in table 1 in the specification.

Furthermore, the conventional p-type GaN becomes re-passivated after experiencing thermal annealing in NH₃ ambient over 500°C, while the present as-grown p-GaN keeps its characteristic after the identical experiment, meaning that Mg in the conventional p-type GaN and Mg in the as-grown p-type GaN are in different states. *See attached Exhibit A (Article of which two of the authors are the inventor of the present invention).*

As such, the convention p-type GaN using activation is different from the as-grown p-GaN using NH₃ and Hydrazine as nitrogen source because they have completely different

properties, and the present device of the Group I claims resulted uniquely from the present process of the Group II claims. Therefore, the Groups I and II are not distinct.

The Examiner's position set forth in the Action that Applicant's traversal of this requirement for election on the ground that different embodiments of the same invention are presented may be considered an admission in a subsequent prior art rejection on the ground that one species is obvious in view of the other, is believed improper and contrary to the law. It is believed clear that Applicant's teaching of equivalency in Applicant's own specification is not available to the Examiner as an admission in a rejection under 35 USC 103. The equivalence must be disclosed in the prior art. Any disclosure of equivalence in Applicant's specification cannot be used by the Examiner to support his rejection. See In re Ruff et al., 256 Fed. 2d. 590, 118 USPQ 340. Therefore, this portion of the Action represents an improper use of Applicant's disclosure and Applicant's traversal of this election requirement cannot be used against Applicant in future prosecution of this application.

This response does not present any new matter. Accordingly, as all requirements of the Action have been complied with, an action on the merits and a Notice of Allowance are hereby respectfully solicited.

In light of the aforementioned amendments and discussion, Applicant respectfully submits that the application is now in condition for allowance.

If any issue regarding the allowability of any of the pending claims in the present application could be readily resolved, or if other action could be taken to further advance this application such as an Examiner's amendment, or if the Examiner should have any questions regarding the present amendment, it is respectfully requested that the Examiner please telephone Applicant's undersigned attorney in this regard.

Application of: Tae-Kyung Yoo
Serial No.: 10/563,269
Response to Restriction Requirement

Respectfully submitted,

Date: August 8, 2008



Changhoon Lee
Reg. No. L0316
Husch Blackwell Sanders LLP
720 Olive Street, Suite 2400
St. Louis, MO 63101
314-345-6000
ATTORNEYS FOR APPLICANT



As-grown p-type GaN growth by dimethylhydrazine nitrogen precursor

Eun-Hyun Park*, Joong-Seo Park, Tae-Kyung Yoo

EpiValley, Co., Ltd., 51-2, Neungpyeong-Ri, Opo-Eup, Kwangju City, Kyunggi-Do, Republic of Korea

Available online 18 October 2004

Abstract

A new method for the as-grown p-type GaN layer is reported by employing dimethylhydrazine as a new nitrogen precursor. The results of SIMS and Hall-effect measurement show that the hole concentration and mobility of the as-grown p-type GaN are higher than those of the post-activated conventional p-GaN samples, with 2–3 times lower Mg concentration. Light-emitting diode device results also show better performances in optical power by 10% and reverse breakdown voltage by 20% while maintaining low V_f and I_r . The as-grown p-type layer turns out to remain as p-type after a reverse annealing under ($\text{NH}_3 + \text{H}_2$) at 800 °C for 10 min, and this result is very different from the previous works.

© 2004 Elsevier B.V. All rights reserved.

PACS: 81.05.Eq; 81.15.Gh; 72.80.Eg; 71.55.Eq

Keywords: A3. Metalorganic vapor phase epitaxy; B1. Nitrides; B2. Semiconducting III–V materials; B3. Light-emitting diodes

1. Introduction

GaN-based III–V semiconductors have become a promising material for short-wavelength optoelectronic devices because of their large and direct band gap energy. The realization of p-type GaN layer was a key barrier to lead GaN material to the commercial market from the laboratory. General methods for changing Mg-doped GaN layer to p-

type are post-activation such as thermal annealing in N_2 ambient [1] and low-energy electron beam irradiation (LEEBI) [2]. The thermal annealing method is more commonly used because of its simplicity. A well-known reason for the necessity of the post-activation process is to resolve the hydrogen passivation of the Mg acceptor. The post-activation process breaks the H–Mg complex bonding and extracts the H radical from the p-GaN layer. Although there have been some efforts to reduce H–Mg complexes in the p-GaN layer by minimizing the quantity of hydrogen carrier gas during p-GaN growth [3,4], the main origin of

*Corresponding author. Tel.: +82-31-767-0300; fax: +82-31-767-0316.

E-mail address: chpark@epivalley.com (E.-H. Park).

hydrogen passivation is the H radical from NH_3 dissociation instead of H_2 [5]. Therefore, the H radical from NH_3 dissociation should be substantially minimized or removed in order to obtain the as-grown p-type layer fundamentally.

In this report, the as-grown p-type GaN layer is achieved by using dimethylhydrazine (DMHy) as the nitrogen precursor. To confirm the realization of the as-grown p-type GaN, several verification tests such as photoluminescence (PL), Hall-effect measurement and SIMS have been carried out. In addition, light-emitting diode (LED) devices with the as-grown p-type GaN layer have been fabricated, and the results have been compared with the conventional LED sample. The mechanism of the as-grown p-type GaN layer by DMHy is explained in the Discussion section.

2. Experiments

The epitaxial layers were grown with a multi-wafer metal organic chemical vapor deposition (MOCVD). Trimethylgallium (TMGa) and trimethylindium (TMIn) were used as Ga and In precursors, respectively. Bis-cyclopentadienylmagnesium (Cp_2Mg) was utilized as a p-type dopant. The p-GaN layer was grown in the ambient of a mixture of DMHy and NH_3 . Other layers such as U-GaN, N-GaN and MQW were grown in NH_3 ambient.

Hydrazine sources such as DMHy and tertiarybutylhydrazine (TBHy) have higher cracking efficiency at low temperature compared with NH_3 . Therefore, these sources can be applied to the low-temperature GaN or InGaN layers growth [6,7]. In these experiments, however, p-GaN layers were grown at over 1000 °C in the same condition as the conventional p-GaN layer with NH_3 in order to directly compare the results.

It seems that the H_2 mixture in the carrier gas reduces the carbon contamination from $(\text{CH}_3)_\text{N}$ radical [6]. The film grown by DMHy shows an absorption of C–N and C=N in the FT-IR spectra. In these experiments, we also found out that the carbon contamination reduces the hole concentration and degrades the crystal quality of the p-GaN layer. However, the carbon contamination

can be efficiently reduced by mixing H_2 in the carrier gas.

The room temperature Hall-effect, PL and SIMS measurements were conducted for the evaluation of p-GaN layers with DMHy and NH_3 . To find out the effects of the as-grown p-type GaN layer in LED performances, LED devices were fabricated.

3. Measurements

3.1. Hall-effect measurement

Van der Pauw's method was used to measure the Hall-effect characteristics of 1 μm p-GaN on 0.5 μm U-GaN. To avoid the argument about the possibility of activation during the contact metal alloy, we did not perform the alloy of the contact metal. The ohmic contact was obtained without the alloy. The conventionally grown p-GaN layer with NH_3 was activated using thermal annealing in nitrogen ambient. The p-GaN sample with the DMHy nitrogen precursor was not post-activated. The results of Hall-effect measurement are shown in Table 1. Two samples were grown in the same condition except the nitrogen precursor. The sample using DMHy shows 2–3 times higher hole mobility than that of the conventionally grown sample. Also, the hole concentration of the DMHy sample is higher than that of the NH_3 sample. These results support the fact that the as-grown p-type layer is obtained by the DMHy nitrogen precursor, even without the post-activation. The principle of the as-grown p-type GaN by DMHy is explained in the Discussion section.

Table 1

The Hall-effect measurement results of the conventional P-GaN layer with post-activation and the as-grown P-GaN layer without post-activation

P-GaN condition	Conventional P-GaN	As-grown p-type GaN
Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	8~15	20~30
Hole concentration (cm^{-3})	$1\sim3\cdot10^{17}$	$3\sim4\cdot10^{17}$

3.2. PL measurement

The room temperature PL results of p-GaN layers with NH_3 and DMHy are shown in Figs. 1 and 2, respectively. As shown in Fig. 1a, the conventional p-GaN layer with NH_3 shows stronger yellow band emission compared with the main peak at 439 nm. However, the yellow band begins to shrink with the progress of post-activation. The main peak intensity between 430 and 450 nm increases due to the strong transition from the conduction to the impurity level. Fig. 1b shows the PL characteristic of the

fully post-activated conventional p-GaN layer. This is the normal phenomenon in the conventional p-GaN layer with NH_3 . Nevertheless, as shown in Fig. 2a, the main peak intensity in the as-grown p-type GaN layer is much stronger compared with the yellow band without the post-activation process. Although thermal post-activation is done on the as-grown p-GaN layer, there is no change in the spectrum shapes as shown in Fig. 2b. As a result, the as-grown p-type GaN layer with DMHy shows PL characteristics similar to the sufficiently post-activated conventional p-GaN layer.

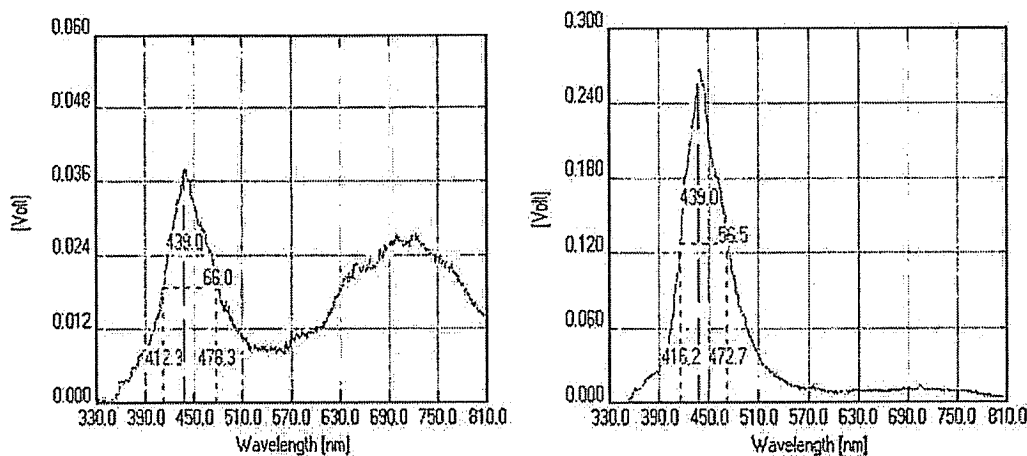


Fig. 1. Shapes of PL spectra of the conventional p-GaN layer with NH_3 : (a) before post-activation, (b) after post-activation.

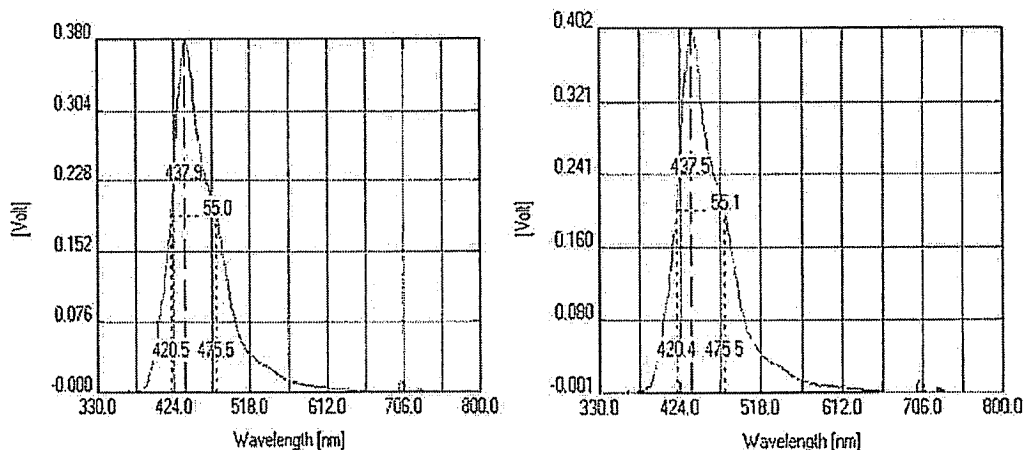


Fig. 2. Shapes of PL spectra of the as-grown p-type GaN layer with DMHy: (a) before post-activation, (b) after post-activation.

3.3. SIMS measurement

The relative Mg concentration of the as-grown p-GaN layer is compared with that of the conventional p-GaN layer. The thickness of p-GaN is 0.3 μm on 1 μm U-GaN. There is an initial low Mg-doped p-GaN layer ($\sim 0.05 \mu\text{m}$) between U-GaN and highly doped p-GaN layer (0.3 μm) in order to improve the surface morphology. From the SIMS results in Fig. 3, it is disclosed that the relative Mg concentration of

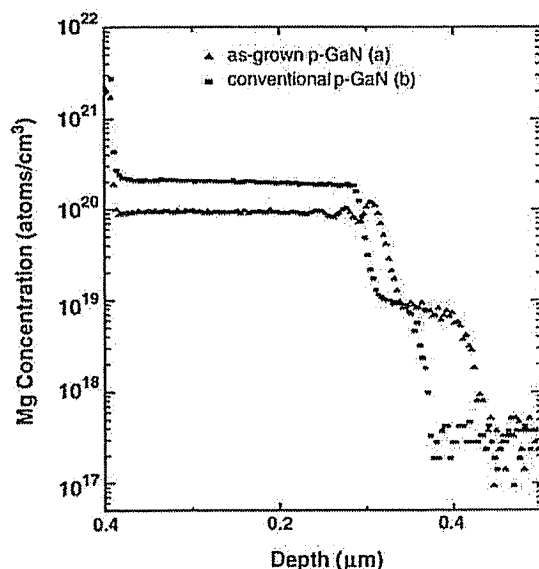


Fig. 3. SIMS results of the relative Mg concentration of P-GaN layers by (a) DMHy and (b) NH_3 .

the DMHy sample is 2 to 3 times lower than that of the NH_3 case, while the hole concentration and mobility of the DMHy sample are higher than those of the NH_3 sample as mentioned in the Hall-effect measurement. These results indicate that the Mg efficiency to hole carrier in the DMHy sample is higher. Therefore, it is possible to achieve a higher hole concentration with a lower Mg concentration. It is thought that the higher hole mobility of the DMHy sample comes from the improved crystal quality due to the lower Mg concentration.

3.4. LED devices

The as-grown p-type GaN layer applied to the conventional LED device structure. Because electrical characteristics such as forward voltage (V_f), reverse leakage current (I_r) and reverse breakdown voltage (V_r) are very sensitive to P-GaN qualities, the device level test is a proper method to evaluate the p-GaN layer. As shown in Table 2, three kinds of samples were prepared to compare the performances of the as-grown p-type LED with the conventional LED. Sample (a) is the conventional LED device with the post-activation step. Samples (b) and (c) are the as-grown p-type LED without the post-activation step. Samples (b) and (c) were cooled down in ($\text{NH}_3(10\text{L}) + \text{H}_2$) and ($\text{NH}_3(10\text{L}) + \text{N}_2$) ambient, respectively. The NH_3 flow in the cooling step of both samples is to exclude the possibility of in situ activation during

Table 2

LED results of the conventional LED with the post-activation (sample (a)), the as-grown p-type LED cooled in the ($\text{NH}_3 + \text{H}_2$) ambient (sample (b)), the as-grown p-type LED cooled in ($\text{NH}_3 + \text{N}_2$) ambient (sample (c)), and the as-grown p-type LED re-annealed in the ($\text{NH}_3 + \text{H}_2$) ambient at 800 $^\circ\text{C}$ for 10 min (sample (d))

	sample (a)	sample (b)	sample (c)	sample (d)
Nitrogen precursor	NH_3	DMHy + NH_3	DMHy + NH_3	DMHy + NH_3
Cooling condition	($\text{NH}_3 + \text{H}_2$)	($\text{NH}_3 + \text{H}_2$)	($\text{NH}_3 + \text{N}_2$)	($\text{NH}_3 + \text{N}_2$)
Post-activation	O	X	X	X
Post-annealing	X	X	X	Thermal annealing in ($\text{NH}_3 + \text{N}_2$) ambient @ 800 $^\circ\text{C}$, 10 min
V_{f1} @ 20 mA	3.1 V	3.12 V	3.13 V	3.14 V
V_{f2} @ 10 μA	2.35 V	2.41 V	2.37 V	2.39 V
V_{f3} @ 5 mA	2.78 V	2.79 V	2.8 V	2.81 V
I_r @ -5 V	0.01 μA	0.02 μA	0.02 μA	0.00 μA
V_r @ -10 μA	20 V	23.6 V	24 V	26.7 V
P_{out} (PD current)	12 μA	12.6 μA	13.3 μA	13.5 μA

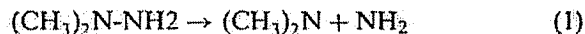
the cooling process of MOCVD. It had already been proven that the activation does not occur in NH_3 cooling ambient [1]. The device results of samples (b) and (c) show improved LED performances compared with the conventional LED device (sample (a)), as shown in Table 2. The cooling conditions do not affect LED results. The reverse breakdown voltage is improved by 20% due to the lower Mg concentration. The optical output power (P_{out}) is also improved by 10% due to the higher hole concentration. As shown in the Hall-effect and SIMS measurement, the relatively lower Mg concentration of the as-grown p-type GaN layer can relax the crystal degradation by heavy impurity doping. The forward current–voltage characteristics of the as-grown p-type LEDs are similar to the conventional LED results.

With the as-grown p-type LED wafer (sample (b)), the thermal treatment in NH_3 ambient (NH_3 : 10L; H_2 : 10L; @850 °C, 10 min) was done to test the re-passivation of Mg with H radical. When the post-activated conventional p-GaN layer experiences thermal annealing in NH_3 ambient over 500 °C [8], it is passivated again with H radical and then becomes a highly resistive layer. However, as shown in Table 2 (sample (d)), the as-grown p-type LED showed almost identical results before and after thermal annealing in NH_3 . These results mean that the as-grown p-type GaN has the stronger p-type characteristic than the post-activated p-type LED in the re-passivation problem.

4. Discussion

The Mg-doped GaN layer which is grown in NH_3 and H_2 ambient shows very high resistivity due to hydrogen passivation. As explained in some reports [3,4], the reduction of H_2 flow during p-GaN layer growth is the positive direction to reduce H–Mg complex formation. However, because the H–H bonding in hydrogen (104 kcal/mol) is stronger than N–H bonding in ammonia (93.3 kcal/mol) [8], the H radical from NH_3 is the main origin of the H–Mg complex in the p-GaN layer. Therefore, in this research, a method to minimize H radical generation from NH_3 is developed.

In DMHy ($(\text{CH}_3)_2\text{N-NH}_2$), the N–N bonding is easily broken over 400 °C due to its low free energy change (33.4 kcal/mol)[6,9]. When the N–N bonding is broken, NH_2 and $(\text{CH}_3)_2\text{N}$ radicals are generated. The pyrolysis of DMHy occurs in two steps:



As shown in reactions Eqs (1) and (2), NH_2 and CH_3 radicals are generated as the by-products of the pyrolysis of DMHy. The NH_2 radical is highly reactive and recombines immediately with the ambient H radical to form NH_3 with stable bond structure. Likewise, the CH_3 radical easily combines with the H radical to form the CH_4 structure.



Because these reactions can reduce the H radical in p-GaN growth ambient, H–Mg complex formation can be minimized in the p-GaN layer. The analysis results of gas products formed from the decomposition of DMHy [9] support our explanation on the mechanism of the as-grown p-type GaN with DMHy. According to this report, NH_3 and CH_4 are predominant in the pyrolysis products of DMHy. In conclusion, DMHy nitrogen precursor does not generate the H radical, and the by-products such as NH_2 and CH_3 absorb the H radical in ambient. Therefore, the as-grown p-type GaN layer could be achieved by minimizing the quantity of H radical in the p-GaN growth ambient.

5. Summary

A new method for the as-grown p-type GaN layer is developed by employing DMHy. In the Hall-effect measurement, the as-grown p-type sample shows higher hole concentration and mobility than the conventional p-GaN layer. SIMS analysis shows that the Mg concentration in the as-grown p-type GaN is 2–3 times lower than that of the conventional p-type GaN layer grown by NH_3 . In the PL measurement, the spectrum shapes of the as-grown p-type GaN are

similar to the fully post-activated conventional p-GaN layer. LED devices with the as-grown p-type layer also show better performances in reverse breakdown and optical power, while maintaining low V_f and I_f . The as-grown p-type layer turns out to remain in p-type GaN after $(\text{NH}_3 + \text{H}_2)$ annealing at 800 °C for 10 min, and this result is very different from the previous researches. The mechanism of the as-grown p-type is that NH_2 and CH_3 radicals from the pyrolysis of DMHy absorb the H radical in the growth ambient and minimize H–Mg complex formation during the growth.

Acknowledgements

The authors would like to thank Dr. D.J. Kim at Samsung Electro-Mechanics Co., Ltd. for the helpful comments and SIMS measurement.

References

- [1] S. Nakamura, T. Mukai, M. Senoh, N. Iwasa, *Jpn. J. Appl. Phys.* 31 (1992) L139.
- [2] H. Amano, M. Kito, K. Hiramatsu, I. Akasaki, *Jpn. J. Appl. Phys.* 28 (1989) L2112.
- [3] L. Sugiura, M. Suzuki, J. Nishio, K. Itaya, Y. Kokubun, M. Ishikawa, *Jpn. J. Appl. Phys.* 37 (1998) 3878–3881.
- [4] S. Yamaguchi, Y. Iwamura, Y. Watanabe, M. Kosaki, Y. Yukawa, S. Nitta, S. Kamiyama, H. Amano, I. Akasaki, *J. Crystal Growth* 248 (2003) 503–506.
- [5] S. Nakamura, N. Iwasa, M. Senoh, T. Mukai, *Jpn. J. Appl. Phys.* 31 (1992) 1258.
- [6] Y.J. Hsu, L.S. Hong, K.F. Huang, J.E. Tsay, *Thin Solid Films* 419 (2002) 33–39.
- [7] Y.J. Hsu, L.S. Hong, J.E. Tsay, *J. Crystal Growth* 252 (2003) 144–151.
- [8] J. Emsley, *The Elements*, Oxford University Press, New York, 1991.
- [9] E. Bourret-Courchesne, Q. Ye, D.W. Peters, J. Arnold, M. Ahmed, S.J.C. Irvine, R. Kanjolia, L.M. Smith, S.A. Rushworth, *J. Crystal Growth* 217 (2000) 47–54.